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SRCC REPORT NO. 154

UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA

JULY 14, 1971

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The Center is supported by an Institutional Grant (NsG-416) from the National Aeronautics and Space Administration, strongly supplemented by grants from the A. W. Mellon Educational and Charitable Trust, the Maurice Falk Medical Fund, the Richard King Mellon Foundation and the Sarah Mellon Scaife Foundation. Much of the work described in SRCC reports is financed by other grants, made to individual faculty members.

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Abstract

Reaction rates of NO^+ and its hydrates, $NO^+ \cdot nH_2O$ (n = 1-3), with water were measured in a flow system. The mechanism for conversion of NO^+ hydrates to H_3O^+ hydrates was confirmed, and rate constants for the sequence of six clustering, redissociation, and rearrangement reactions were determined for each of the four carrier gases He, Ar, N_2, and O_2.

I. INTRODUCTION

Ever since the first mass spectrometer measurements of the ionospheric D region positive ion composition by Narcisi and Bailey[1], there has been a great deal of interest in the rates and mechanism of hydration of NO^+, O_2^+, and H_3O^+. The observation of H_3O^+ and its first hydrate, and the large contribution to the total ion density by ions of mass greater than 45amu stimulated speculation on the role which water vapor plays in D-region chemistry. A subsequent flight[2] with a mass spectrometer capable of detecting heavier ions showed $H_3O^+ \cdot 2\,H_2O$, $O_2^+ \cdot H_2O$ and $NO^+ \cdot H_2O$ to be present.

Fehsenfeld and Ferguson[3] first proposed a mechanism which could

account for the formation of hydronium ions by the reactions of O_2^+ and NO^+ with water vapor. This mechanism has been confirmed by Good *et al.*[4] for O_2^+ and by Lineberger and Puckett[5] for NO^+. The reaction sequence for NO^+ is thought to be

$$NO^+ + H_2O + M \xrightarrow{k_1} NO^+ \cdot H_2O + M \qquad (1)$$

$$NO^+ \cdot H_2O + H_2O + M \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} NO^+ \cdot 2\,H_2O + M \qquad (2)$$

$$NO^+ \cdot 2\,H_2O + H_2O + M \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} NO^+ \cdot 3\,H_2O + M \qquad (3)$$

$$NO^+ \cdot 3\,H_2O + H_2O \xrightarrow{k_4} H_3O^+ \cdot 2\,H_2O + HNO_2 \qquad (4)$$

The omission of the reverse of reaction (1) does not imply that it does not occur, but simply that its equilibrium strongly favors the formation of hydrate under all experimental conditions investigated in this work. In the present study, the above six rate constants were determined in an ion-molecule reaction flow system using four carrier gases, He, Ar, N_2, and O_2. The results were examined for their internal consistency as well as for the reasonableness of their absolute magnitudes.

II. EXPERIMENTAL

The flowing afterglow system has been described previously[6]. All measurements were made at 296°K and within a pressure range of 0.2 to 1.4 Torr.

The carrier gases, O_2 (extra dry), N_2 and Ar (prepurified), and He (high purity) were purified by passage through a trap containing Union Carbide 13X molecular sieve which was cooled to 77°K for He and to 196°K for O_2,

N_2, and Ar. This decreased the impurity ion levels by more than an order of magnitude. Cylinder NO(C.P. grade) was used after being passed through a dry ice-isopropanol trap.

NO^+ ions were formed by adding a small flow of NO ($\lesssim$ 2% of total) to the carrier gas downstream from the electron impact ionizer. Rapid charge-transfer reactions produced NO^+ which completely dominated the ion spectrum in the reaction zone. A minor peak observed at 60amu was $(NO)_2^+$ which was formed by the reaction

$$NO^+ + NO + M \rightarrow (NO)_2^+ + M$$

but which was greatly reduced by the fast switching reaction

$$(NO)_2^+ + H_2O \rightarrow NO^+ \cdot H_2O + NO$$

when water was added.

After the addition of NO to the ionized carrier stream, the measured NO^+ ion current was observed to decrease by several orders of magnitude over a two hour period. The reduction in the number of detected ions was overcome by putting a small negative potential of about 2 V on the metal cone through whose orifice the ions were sampled. Experiments in which this draw-out voltage was varied from 0 to 2 V showed that it had no effect on the ion kinetics.

The quadrupole mass filter was operated at very low resolution to maintain uniform transmission across the mass range since the kinetic analysis of the data is quite sensitive to mass discrimination. A check was made on mass discrimination by monitoring all of the detectable ions in the clustering sequence, including the hydrogen cluster ions not shown in Figures 1 and 2. The sum of the currents for all of the ions remained

constant to within 10 - 20% as the reaction zone (time) was lengthened and the ion spectrum was converted from predominantly light ions, NO^+, to the heavier ions $H_3O^+ \cdot nH_2O (n=2-4)$.

III. DATA ANALYSIS AND RESULTS

Rate constants for the NO^+ clustering sequence were obtained using two types of analysis. The rate constant for the initial step, k_1, was derived from semilog plots of the parent ion current, i_{NO^+}, as a function of z, the position of the movable injector using the conventional flowing afterglow analysis.[6-9]

The rate constants for the subsequent steps were obtained by fitting computed curves of the z-dependence of ions NO^+, $NO^+ \cdot H_2O$, $NO^+ \cdot 2H_2O$, and $NO^+ \cdot 3H_2O$ to experimental data. For a given set of laboratory conditions, carrier pressure, water pressure, and flow velocity, the ion currents for masses 30, 48, 66, and 84 were measured for each of 6 to 10 different positions of the water injector along the reaction zone (from z = 20 to 70cm). Typical data are shown in Figures 1 and 2. Using a Runge-Kutta numerical integration of the simultaneous differential rate equations for the six reactions, (1) through (4), computed ion concentrations were obtained. In the computation the laboratory conditions of flow velocity, water pressure, and total pressure are fixed; k_1 was obtained from the semilogarithmic decay of NO^+; and the rate constants k_2, k_{-2}, k_3, k_{-3} and k_4 were varied to give the best fit to the experimental data. The computer calculations were carried out at a remote terminal using the University of Pittsburgh time sharing system. The results of a test computation were compared to the experimental data, and then an adjusted set of rate constants would be tried in order to get an improved fit. With this

procedure it was possible to make 10 to 15 trial fits in an hour at a cost of approximately 20 to 25sec of computer time (IBM 360/50) per fit. Typical "best" fits of experimental data are shown in Figures 1 and 2. While only a very narrow range of values for the bimolecular rate constant, k_4, would provide a good fit of the data, the forward-reverse pairs k_2, k_{-2} and k_3, k_{-3} could be varied over a large range to produce equally good fits. Most of the data, particularly those taken at large water concentrations ($> 10^{-3}$ Torr) could be fitted with no reverse reactions in the scheme. As a small reverse rate constant was introduced the forward rate constant had to be increased to compensate for the back reaction and to maintain the concentration level of the species. Since the magnitude of the necessary increase in forward rate constant depended on the experimental conditions, it was possible to combine the k(forward), k(reverse) data from a number of different experiments in a single carrier gas to determine a pair of constants which would optimize the fit of all the data. An example of this analysis is illustrated in Figure 3 where k_{-3} has been plotted as a function of k_3 for all of the experiments with He carrier. Data from three experiments intersect at a point which corresponds to the single value of k_3 and k_{-3} which will fit all three experiments and the points from a fourth pass within the range of the error limits of the determination.

A test of this procedure is the constancy of the equilibrium constants, $K_2 = k_2/k_{-2}$ and $K_3 = k_3/k_{-3}$, since they are independent of the carrier gas used. The equilibrium constant, K_3, was the same to within a few percent in the four carrier gases. K_2 was determined with less accuracy because the very small magnitude of the reverse rate, k_{-2}, made it the least important parameter in the analysis.

The equilibrium constants K_2 (8×10^{-14} cm^3) and K_3 (1.1×10^{-15} cm^3)

are nearly equal to the values which Searles and Kebarle[10] have reported for the analogous steps in the clustering of K^+ ions with water. If one assumes the same entropy changes in the two similar processes, the binding energies for the second and third water molecules on NO^+ can be estimated to be about 16 and 13 kcal/mole, respectively.

In Ar, O_2, and N_2 carrier, the measured rate constants were found to be somewhat pressure dependent. In these gases the rate constants were larger at low carrier pressures (0.2 Torr) than at high pressures (0.6 Torr) where they leveled off with increasing pressure. The discrepancy of about 10% in O_2 and N_2 was not considered to be a serious problem. However, in Ar the difference was about 40% and it was necessary to understand its origin in order to reduce the error.

Since the rate constant for the bimolecular reaction

$$\begin{aligned} Ar^+ + H_2O &\rightarrow Ar\,H^+ + OH \\ &\rightarrow H_2O^+ + Ar \end{aligned} \qquad (5)$$

had been previously measured by us in He carrier[6], a study of its pressure dependence in Ar was undertaken to show whether the effect arose only in clustering reactions or was present in all Ar carrier experiments. In these experiments reaction (5) exhibited a similar pressure dependence to that of the clustering reactions and the correct rate constant was obtained only in the low pressure limit. The bimolecular rate constant in the clustering sequence, k_4, should be independent of the carrier gas and good agreement with the value of k_4 in He, O_2, and N_2 experiments was obtained when the low pressure Ar results were used.

Since the Reynolds number for the carrier flow is about an order of magnitude larger in Ar, O_2, and N_2 (R = 100 to 200) than in

He (R = 10 to 20), the possibility that Poiseuille flow was not established in the 70cm entry length to the reaction zone was considered as a source of the pressure dependence in the heavy gases. Direct measurements of the radial velocity profiles were made using a pitot tube. After viscous boundary layer corrections had been applied to the measurements,[11] the profiles agreed to within about 5% with the values calculated from the bulk flow properties (flow rate and tube pressure) assuming a parabolic velocity distribution. Therefore, the assumption of Poiseuille flow is valid for all four carrier gases studied. Further experiments showed that the pressure dependence could be mainly attributed to nonuniform mixing of the water vapor added through the neutral reactant injector. Since the injector is assumed to behave as a planar source in the rate constant analysis[6], slow diffusion-controlled mixing in the heavy carrier gases, N_2, O_2 and Ar, may cause a pressure dependence in the rate constants which is not observed in He. This was tested in experiments where NO was added through the water injector to Ar or He carrier containing some O-atoms and the uniformity of the O + NO chemiluminescence was observed visually. Much poorer mixing was found in Ar than in He and this led to the construction and testing of a greatly improved teflon ring injector of 3cm diameter with 24 evenly spaced holes on its outside and 16 holes on its inside edge.

Our results and those of two other laboratories are shown in Table 1. The work of Fehsenfeld *et al.*[12] was carried out using He, Ar, and N_2 carrier in a flowing afterglow system. Puckett and Teague[13] have recently reported rate constants from a study of NO^+ clustering with H_2O in a stationary afterglow. The agreement of the results from the three laboratories is very good. The general trends are as expected: The three-body recombination rate constants increase about one order of magnitude from n = 1 to

n = 3 where n is the number of H_2O in the product cluster ion; the increase from M = He to N_2 for a given recombination k_n is a factor of three to five; the redissociation rate constants increase two orders of magnitude from n = 2 to 3 due to the weaker binding and greater complexity (internal energy) of the larger (n = 3) ion.

When the recombination k_n are simply interpreted in terms of the scheme, say for k_2,

$$NO^+ \cdot H_2O + H_2O \underset{b}{\overset{a}{\rightleftarrows}} NO^+ \cdot 2\,H_2O^\dagger$$

$$NO^+ \cdot 2\,H_2O^\dagger + M \overset{c}{\rightarrow} NO^+ \cdot 2\,H_2O + M$$

one may reasonably expect k_a to be about $3\times10^{-9}cm^3/sec$ by analogy with our earlier findings[6] for $A^+ + H_2O$ reactions where the rate constant was a factor two to three larger than the Langevin value; and k_c, the energy transfer step, is likely to be about $10^{-9}cm^3/sec$, near its Langevin value, because of the lower polarizability of the neutral reactant and the absence of ion-dipole forces. Taking k_2 for Ar, O_2, or N_2 to be about $10^{-27}cm^6/sec$, one obtains $k_b \sim 10^9 sec^{-1}$ which shows (a) that the recombination is (and should be) in its low-pressure, three-body regime up to quite high pressures, $\gtrsim$ 100 Torr; (b) that the vibrationally excited cluster ion appears to be intermediate between a rigid structure whose lifetime would be in the 10^{-7} to $10^{-8}sec^1$ range and a completely loose structure with many free internal rotations whose lifetime would be in the 10^{-11} to $10^{-12}sec^1$ range.[14] The relatively long lifetime of the energy-rich cluster ion also requires the recombination rate constant to have a strong negative temperature dependence approximately in the T^{-6} or exp(+4kcal/RT) range, which may be important in ionospheric applications. In the simple model of the recombination

process, the M-effect enters only through the stabilization rate constant k_c, and may thus be controlled by the reduced mass and by the polarizability of M. The relative Langevin rate constant ratios would thus be 1:1.2:1.3:1.4 for k_1 and 1:1.1:1.2:1.3 for k_2 in the order He:Ar:O_2:N_2, whereas the experimental ratios are approximately 1:3:3:4, *i.e.* there is good qualitative agreement except for He for which the theory predicts too large a relative rate constant. In all, the recombination and dissociation behavior of these reactions is well characterized by simple rate theory with the possible exception of the detailed mechanism and geometry of the rearrangement reaction (4) which presents intriguing possibilities[12] of linear chain *vs.* spherical ion cluster arrangements.

Acknowledgments

The authors gratefully acknowledge the contributions of Mr. D. L. Doerfler in writing the computer program, and of Dr. A. E. Roche and Miss V. M. Bierbaum in helping with experiments and computations.

* This research was supported by the Advanced Research Projects Agency, The Department of Defense, and was monitored by U. S. Army Research Office-Durham, Box CM, Durham, N. C. 27706, under contract no. DA-31-124-ARO-D-440.

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TABLE 1. NO^+ Clustering Rate Constants

M	k_1 $10^{-29}cm^6/sec$	k_2 $10^{-28}cm^6/sec$	k_{-2} $10^{-15}cm^3/sec$	k_3 $10^{-28}cm^6/sec$	k_{-3} $10^{-13}cm^3/sec$	k_4 $10^{-11}cm^3/sec$	References
He	3.2±0.3[a]	3±0.7	3±1	3.3±0.3	3.0±0.5	7±2	This work
	3.6	3.0	<100	4.0	2.7	8	Ref. 12
Ar	8.5±2	10±4	13±5	12±4	11±5	7±2	This work
	7.8	8.0	<100	15	10	8	Ref. 12
O_2	8.6±1	8±2	10±3	9±2	8±3	7±2	This work
N_2	14±1	12±2	17±5	14±2	14±2.5	7±2	This work
	16	10	<100	20	13	8	Ref. 12
NO	16	11	14	19	19	7	Ref. 13

[a] Error limits on k_1 represent one standard deviation of 10 to 20 experiments but do not include systematic errors. For all other k's they represent a rough estimate of the reproducibility of a small number of computer fits.

FIGURE CAPTIONS

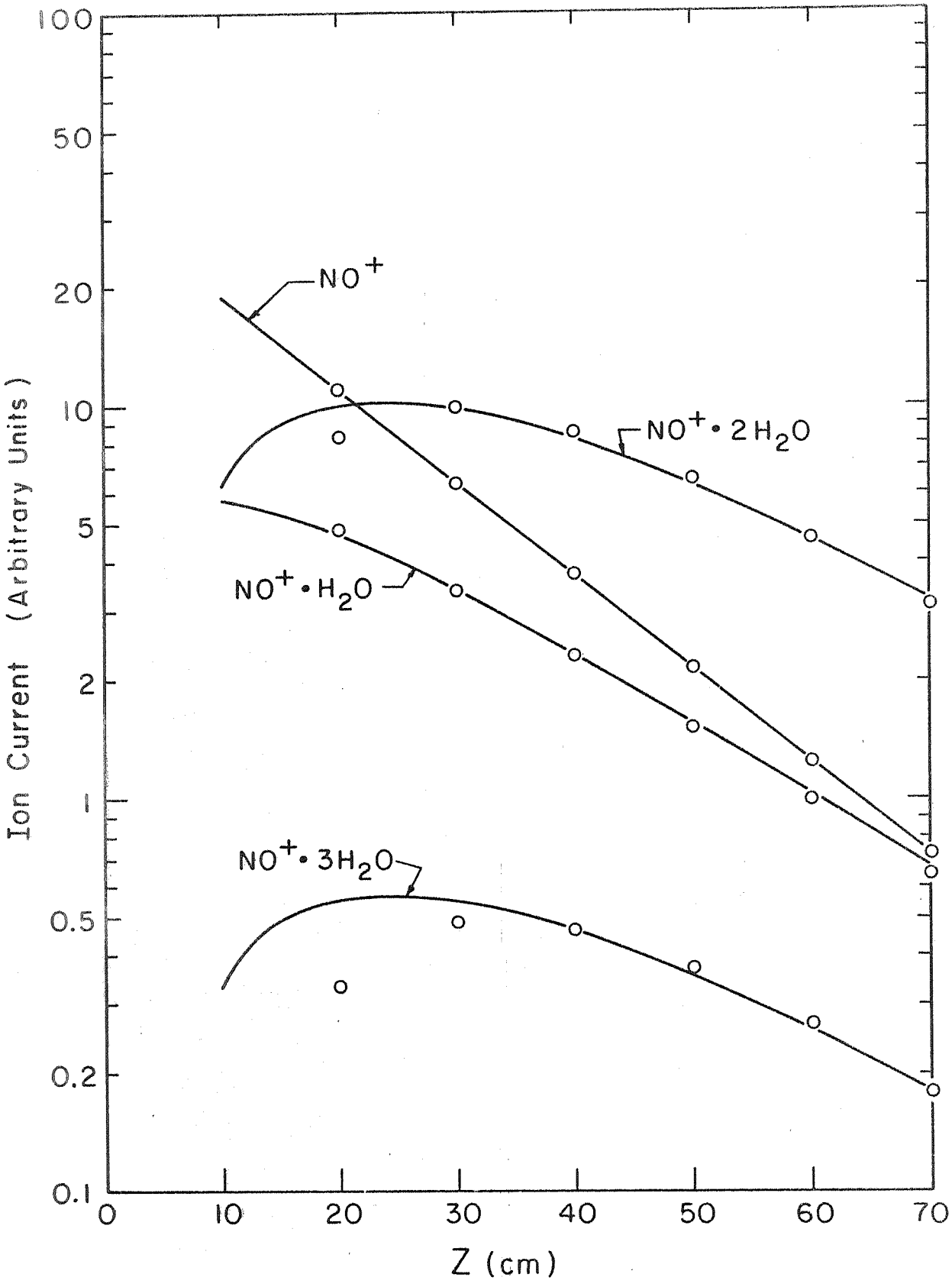
Figure 1 NO^+ Clustering in N_2.
$[N_2] = 2.57 \times 10^{16} cm^{-3}$; $[H_2O] = 8.49 \times 10^{13} cm^{-3}$; $\bar{v} = 3450 cm/sec$

Figure 2 NO^+ Clustering in O_2
$[O_2] = 2.02 \times 10^{16} cm^{-3}$; $[H_2O] = 2.66 \times 10^{14} cm^{-3}$; $\bar{v} = 4210 cm/sec$

Figure 3 Satisfactory computer fits to NO^+ clustering in He with variation of k_3 and k_{-3}

	[He]	$[H_2O]$	$\bar{v}$
	$10^{16} cm^{-3}$	$10^{14} cm^{-3}$	cm/sec
—o—o—	3.37	1.29	5440
—●—●—	4.48	3.18	4270
—□—□—	4.60	4.04	4020
—△—△—	4.60	0.71	4020

Large dotted rectangle indicates range of consistent choice of k_3 and k_{-3} for all four experiments.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NO+
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NO+ • 3H2O
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20
30
40
50
60
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Z (cm)

Figure 1

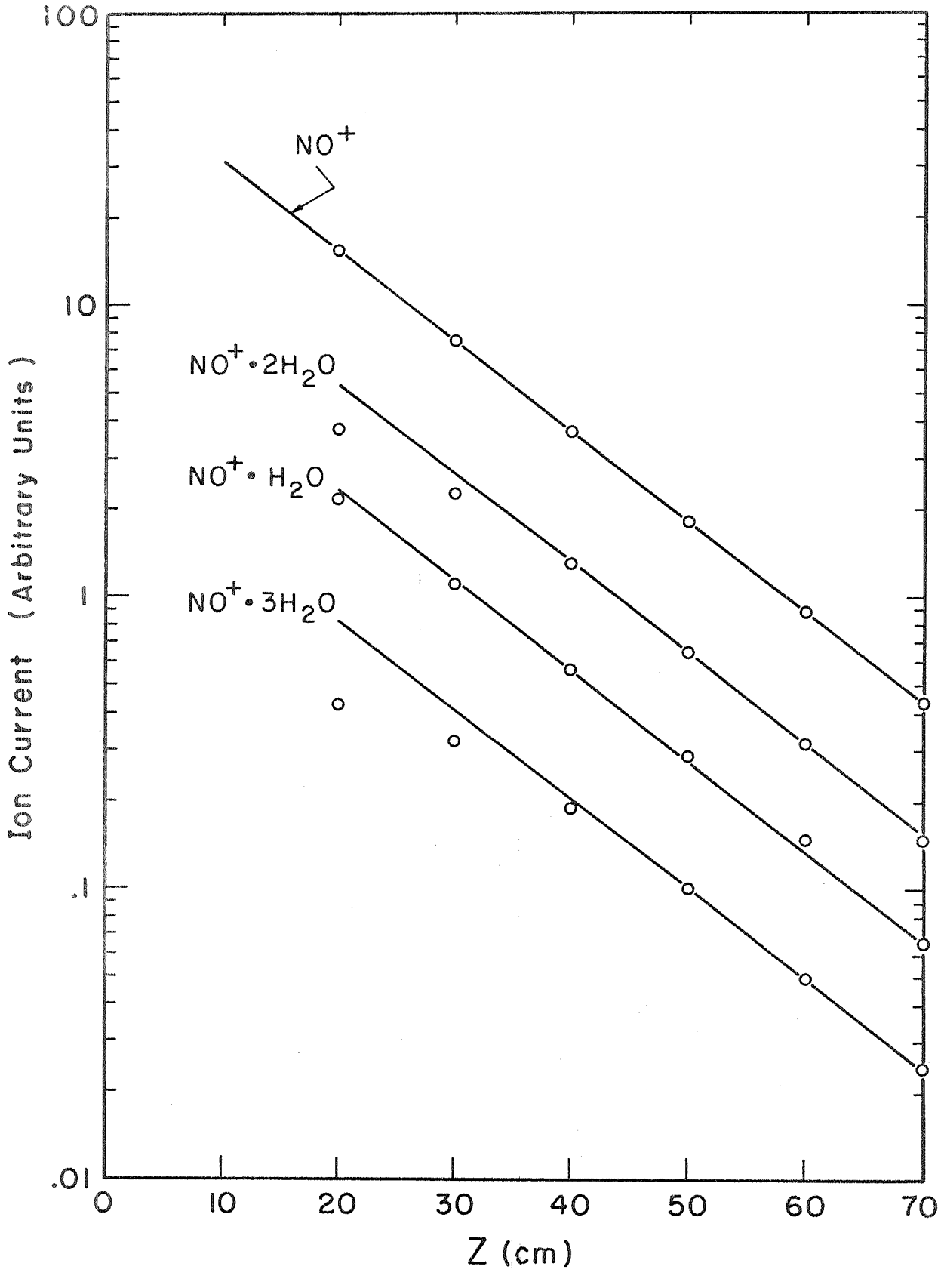
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Figure 2

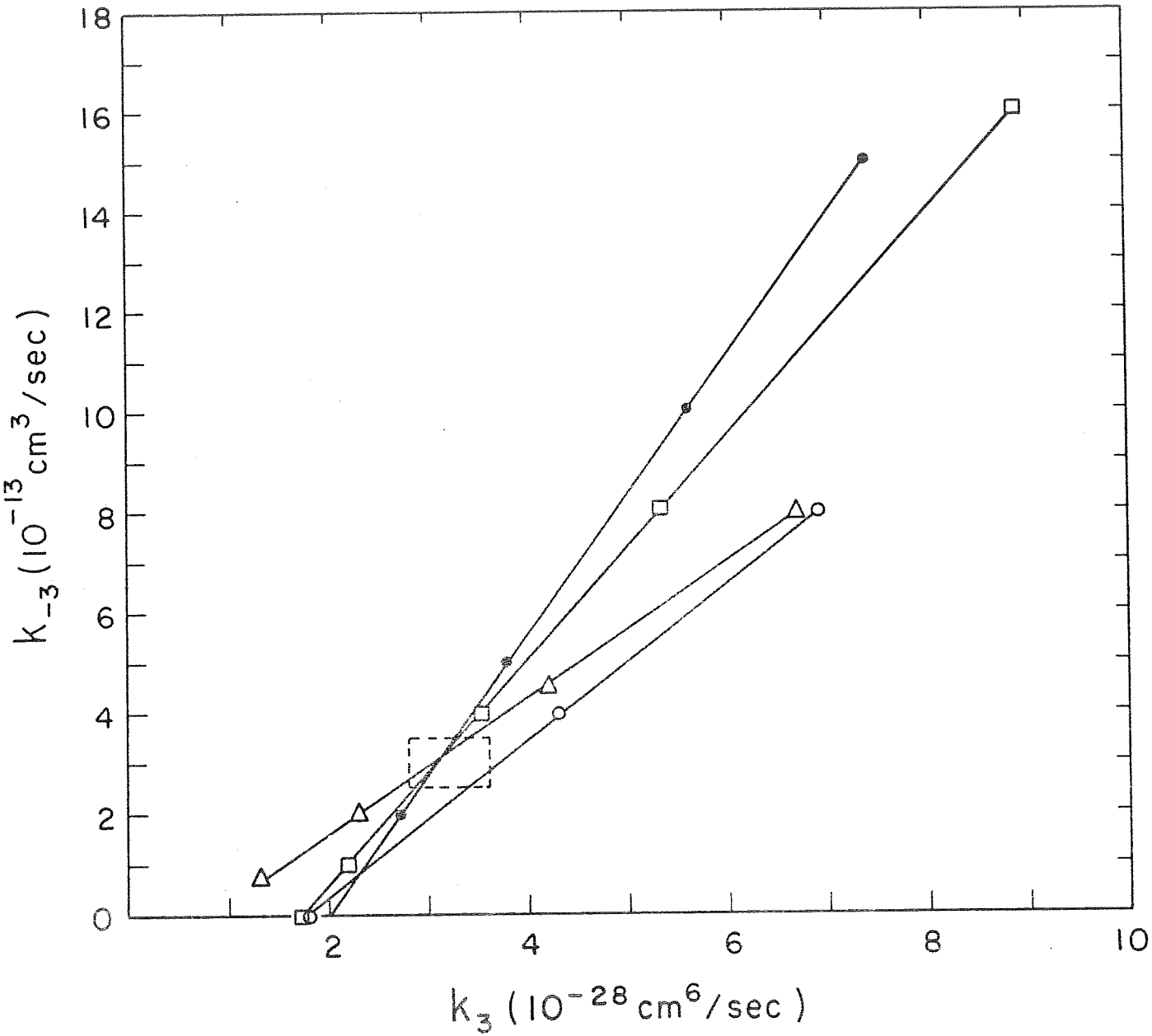

Figure 3